

Measurement of VLE data for propane+1,1-difluoroethane at various temperatures from 268.15 to 333.15 K

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Abstract—Isothermal vapor-liquid equilibrium data for the binary systems of propane (R-290) (1)+1,1-difluoroethane (HFC-152a) (2) were measured at eight temperatures of (268.15, 273.15, 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K), respectively. The experiments were performed with a circulation-type equilibrium apparatus to measure temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were correlated with the Peng-Robinson equation of state (PR-EoS) using the Wong-Sandler mixing rules and the Carnahan-Starling-DeSantis equation of state (CSD EoS). Calculated results showed good agreement with experimental data. It was found that this system has very strong positive azeotropes for all the temperature ranges studied here.

Key words: Propane (R-290), HFC-152a, Vapor-liquid Equilibria (VLE), Carnahan-Starling-DeSantis Equation of State (CSD EoS), Peng-Robinson Equation of State (PR EoS)

INTRODUCTION

Since the Kyoto protocol was announced, many countries have been trying to reduce the emissions of greenhouse gas (GHG). In particular, by 2008-2012, Annex I countries have to reduce their GHG emissions by an average of 5% below their 1990 levels (for many countries, such as the EU member states, this corresponds to some 15% below their expected GHG emissions in 2008). HCFCs and HFCs, which are the replacement of CFC refrigerants, actually have high GWP (global warming potential). As a result, many researchers have conducted experiments to reduce GWP. Light hydrocarbons such as propane, propylene, n-butane, iso-butane have enhanced the value of their usefulness since their good performances are known to the world as natural refrigerants. These are known to be a nice solution for reducing GWP because they are rather cheap, plentiful and eco-friendly chemicals (GWP is very low). However, they are rather toxic, flammable, and explosive. Therefore, mixing light hydrocarbons and HFCs can give a suitable solution of making up for the weakness and show high potentialities to reduce GWP in the future.

Vapor-liquid equilibrium (VLE) data are one of the most important types of information required to evaluate the performance of refrigeration cycles and to determine their optimal compositions. Azeotropic mixtures have merits since their behaviors are similar to pure compounds. However, only limited experimental VLE data containing propane (R-290) have been reported previously in the literature [1-7].

In this work, VLE data for binary mixture of propane (R-290)+1,1-difluoroethane (HFC-152a) at eight temperatures from 268.15 to 333.15 K were measured by using a circulation-type equilibrium

apparatus in which both phases were continuously recirculated. The experimental data were correlated with the Peng-Robinson equation of state (PR EoS) [8] by using the Wong-Sandler mixing rule [9] combined with the NRTL excess Gibbs free energy model and the Carnahan-Starling-DeSantis equation of state (CSD EoS) [10]. In the range of experimental temperature, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined and the relevant parameters were presented. Almost all the calculated values with this model gave good agreement with the experimental data. Azeotropic behavior has been observed in all the experimental conditions.

EXPERIMENTAL

1. Chemicals

High-grade chemicals of HFC-152a and propane were used for VLE measurement. HFC-152a of purity higher than 99.8% mass was supplied by DuPont Industries, U.S.A. Propane supplied by MG Industry, UK had purity higher than 99.8% mass. The purities of the chemicals used in this work were guaranteed by the manufacturers and they were used without any further purification. The purity of each chemical was tested to confirm by using gas chromatograph.

2. Apparatus

Vapor-liquid equilibria were measured in an apparatus in which both vapor and liquid phases were recirculated continuously. This apparatus, which was explained well in our previous works [4-7], is only briefly explained here. A schematic diagram of this apparatus is illustrated in Fig. 1. The equilibrium cell is a 316 stainless steel with an inner volume of about 85 ml. A pair of Pyrex glass

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[‡]This article is dedicated to Professor Chul Soo Lee in commemoration of his retirement from Department of Chemical and Biological Engineering of Korea University.

Table 1. Thermodynamic properties of components [14]

Chemical	Chemical formula	T_c /K	P_c /MPa	ω
Propane (1)	C_3H_8	369.85	4.248	0.1524
HFC-152a (2)	CF_3CHF_2	386.41	4.517	0.2752

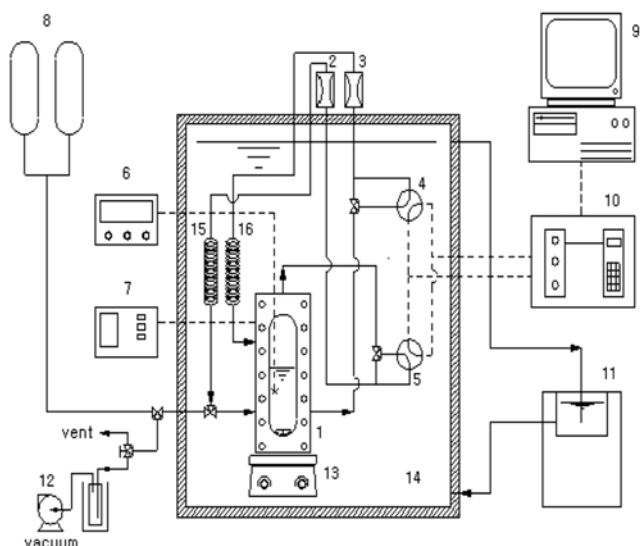


Fig. 1. Schematic diagram of the experimental apparatus.

- | | |
|----------------------------|-------------------------------------|
| 1. Equilibrium cell | 10. Gas chromatograph |
| 2. Vapor circulation pump | 11. Circulator |
| 3. Liquid circulation pump | 12. Vacuum pump |
| 4. Liquid sample valve | 13. Magnetic stirrer |
| 5. Vapor sample valve | 14. Constant temperature water bath |
| 6. Temperature indicator | 15. Vapor phase heat exchanger |
| 7. Pressure indicator | 16. Liquid phase heat exchanger |
| 8. Sample reservoir | |
| 9. Computer | |

windows of cell was installed on two sides of the cell in order to make it possible to observe the inside liquid level and circulating behavior during operation. There is a stirring bar which rotates at various speeds inside the cell. A stirring bar is used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in vapor and liquid phase. The temperature of the equilibrium cell in the bath was maintained by the circulator (HAKKE, Germany) connected to the water bath. The temperature of the sample in the cell was measured with a platinum resistance sensor connected to a digital temperature indicator - F250 precision thermometer model manufactured by Automatic Systems Laboratories Ltd., UK. They were calibrated by NAMAS-accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within 0.01 K, including sensor uncertainty, 0.01 K, temperature resolution, 0.001 K, and measurement uncertainty, 0.001 K. The pressure was measured with a pressure transducer, model XPM60, and digital pressure calibrator indicator - PC106 model manufactured by Beamax, Finland. Pressure calibrations are traceable to national standards (Center for Metrology and Accreditation Certificate Nos. M-95P077 dated 14-11-1995, M-M730 dated 16-11-1995 and M-95P078 dated 16-11-1995); the calibrator uncertainty was 0.0005 MPa, sensor uncertainty was 0.001 MPa, and measurement uncertainty was 0.001 MPa. Therefore, the total uncertainty of the pressure measurement is estimated to be within 0.001 MPa. The vapor and liquid phases in the equilibrium cell were continuously recycled by a dual-head circulation pump, which included a vapor circulation pump and liquid circulation pump powered simultaneously by an electric motor. This pump was manufactured by the Milton Roy Company, USA. The compositions of the sample

were measured by immediately injecting them into the gas chromatograph (Gow-Mac model 550P) by vapor and liquid auto-sampler. This GC was equipped with a thermal conductivity detector (TCD) and a stainless steel column from Restek Company. The signals from GC were processed and converted to data by Autochro Data Module supplied by Young Lin Co., Korea.

3. Procedure

Experiments for a binary system were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of HFC-152a was supplied to the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. Afterward, the proper amount of propane was introduced into the cell from a sample reservoir. The mixture in the cell was stirred continuously with the magnetic stirrer for about 1 hour. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. It is believed that 1 hour or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to the vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. A manometer was used for preparing a standard sample. The two were injected to the manometer and made a mixture. It took more than 2 hours until the two gases were completely mixed and became a standard sample. A micro syringe was used to inject the sample to the GC. These two gases were assumed as ideal gases, so the pressure ratio was approximately equal to its mole fraction here. At least five analyses were performed for each phase and the average values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall accuracy in the measurements of the composition of ± 0.002 in the mole fraction for both the liquid and the vapor phases.

4. Correlation

In this work, the experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EoS) [8] by using the Wong-Sandler mixing rule [9] and the Carnahan-Starling-DeSantis equation of state (CSD-EoS) [10].

5. PR-EoS

The experimental VLE data were correlated with the PR-EoS [8].

$$P = \frac{RT}{v_M - b} - \frac{a(T)}{v_M(v_M + b) + b(v_M - b)} \quad (1)$$

with

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c} \right) \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_c})]^2 \quad (4)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where the parameter a is a function of temperature, b is constant, k is a constant characteristic of each substance, ω is the acentric factor, P (MPa) is the pressure, P_c (MPa) is the critical pressure, T (K) is the absolute temperature, T_c (K) is the critical temperature, and v_M is the molar volume of the mixture.

The Wong-Sandler mixing rules [9] were used in this work to obtain EoS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - \frac{A_\infty^E}{CRT} - \sum_i x_i a_i / RT b_i\right)} \quad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2} [(b - a/RT)_i + (b - a/RT)_j] (1 - k_{ij}) \quad (7)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (8)$$

where C is a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR EoS used in this work. The single adjustable parameter (k_{ij}) for each binary pair is referred to as the Wong-Sandler mixing rule parameter. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model [11]. In this study, we used the nonrandom two-liquid (NRTL) model [12] given by

$$\frac{A_\infty^E}{RT} = \frac{\sum_i \sum_j x_i x_j G_{ij} \tau_{ij}}{\sum_r x_r G_r} \quad (9)$$

Table 2. Comparison of the measured pure component vapor pressures with the database REFPROP 6.01 [14]

Component	T/K	P_{exp} /MPa	P_{ref} /MPa	ΔP	$ \Delta P /P_{exp}$
Propane (1)	268.15	0.399	0.406	-0.007	0.017
	273.15	0.476	0.474	0.002	0.004
	283.15	0.632	0.636	-0.004	0.007
	293.15	0.833	0.836	-0.003	0.004
	303.15	1.079	1.079	0.000	0.000
	313.15	1.366	1.369	-0.003	0.002
	323.15	1.708	1.713	-0.005	0.003
	333.15	2.116	2.116	0.000	0.000
				Ave 0.005	
HFC-152a (2)	268.15	0.226	0.227	-0.001	0.046
	273.15	0.265	0.264	0.001	0.004
	283.15	0.373	0.373	0.000	0.001
	293.15	0.513	0.513	0.000	0.000
	303.15	0.690	0.690	0.000	0.000
	313.15	0.906	0.909	-0.003	0.004
	323.15	1.174	1.177	-0.003	0.003
	333.15	1.497	1.501	-0.004	0.003
				Ave 0.008	

with

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \text{ and } \tau_{ij} = (g_{ij} - g_{ii}) / (RT) \quad (10)$$

where

$$A_{ij} = (g_{ij} - g_{ii}) \quad (11)$$

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both propane and HFC-152a that were used to calculate the parameters for the PR EoS are provided in Table 1. We set the non-randomness parameter, a_{ij} equal to a fixed value of 0.3 for all of the binary mixtures studied here. The parameters of the PR EoS were obtained by minimizing the following objective function.

$$\text{objective function} = \frac{1}{N} \sum_j \left[\left(\frac{P_{j,exp} - P_{j,calc}}{P_{j,exp}} \right) \times 100 \right]^2 \quad (12)$$

6. CSD-EoS

The CSD-EoS [10] is expressed as follows:

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \quad (13)$$

$$\text{where } y = \frac{b}{4V}, \quad V: \text{ molar volume} \quad (14)$$

In case of pure components, the temperature dependence of 'a' and 'b' are represented by the following form:

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \quad (15)$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (16)$$

The coefficients of $\alpha_0, \alpha_1, \alpha_2$ in Eq. (15) and $\beta_0, \beta_1, \beta_2$ in Eq. (16) were cited from REFPROP 5.0 [13].

In the application of CSD-EoS to mixture, there exists the effective molecular parameters a_m and b_m defined by using the following mixing rules:

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \quad (17)$$

$$b_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij} \quad (18)$$

When $i=j$, the values of a_{ii} and b_{ii} are those of 'a' and 'b' of the pure components which are determined by Eq. (15) and (16). The values of a_{12} and b_{12} can be expressed as the following:

$$a_{12} = (1 - f_{12})(a_{11} a_{22})^{1/2} \quad (19)$$

$$b_{12} = \frac{1}{8}(b_{11}^{1/3} + b_{22}^{1/3})^3 \quad (20)$$

The model involves the adjustable binary parameters, f_{12} , which must be determined from experimental data. In the CSD-EoS calculation, the same objective function that was used in the PR-EoS calculation was used.

RESULTS AND DISCUSSION

A comparison of measured vapor pressures of pure HFC-152a and propane with those calculated from the database REFPROP 6.01 [14], which is considered to be reliable for the pure compounds considered and consistent with literature data, is shown in

Table 3. Vapor-liquid equilibrium measurements for the propane+HFC-152a system

Experimental data			PR EoS				CSD EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$
T/K=268.15										
0.226	0.000	0.000	0.227	0.000	-0.001	0.000	0.220	0.000	0.006	0.000
0.357	0.177	0.368	0.357	0.404	0.000	-0.036	0.381	0.477	-0.024	-0.109
0.380	0.261	0.465	0.380	0.461	0.000	0.004	0.411	0.536	-0.031	-0.071
0.401	0.356	0.536	0.401	0.520	0.000	0.017	0.431	0.578	-0.030	-0.042
0.429	0.512	0.644	0.429	0.617	0.000	0.027	0.449	0.629	-0.020	0.015
0.435	0.564	0.664	0.436	0.649	-0.002	0.015	0.452	0.647	-0.017	0.018
0.439	0.602	0.681	0.440	0.672	-0.001	0.009	0.455	0.660	-0.016	0.021
0.445	0.635	0.687	0.444	0.692	0.001	-0.005	0.456	0.673	-0.011	0.014
0.450	0.673	0.696	0.447	0.715	0.003	-0.019	0.457	0.689	-0.007	0.007
0.456	0.741	0.727	0.450	0.755	0.006	-0.028	0.457	0.723	-0.001	0.004
0.448	0.796	0.703	0.450	0.788	-0.002	-0.085	0.454	0.758	-0.006	-0.055
0.447	0.859	0.735	0.447	0.827	0.000	-0.092	0.447	0.808	0.000	-0.073
0.399	1.000	1.000	0.405	1.000	-0.009	0.000	0.406	1.000	-0.007	0.000
T/K=273.15										
0.265	0.000	0.000	0.263	0.000	0.002	0.000	0.264	0.000	0.001	0.000
0.355	0.080	0.284	0.357	0.298	-0.002	-0.014	0.378	0.330	-0.023	-0.045
0.421	0.158	0.428	0.418	0.431	0.003	-0.003	0.442	0.452	-0.021	-0.024
0.486	0.300	0.551	0.485	0.551	0.001	0.000	0.500	0.548	-0.014	0.003
0.518	0.441	0.623	0.520	0.618	-0.002	0.005	0.525	0.599	-0.007	0.024
0.533	0.537	0.662	0.534	0.653	-0.001	0.009	0.535	0.630	-0.002	0.032
0.543	0.649	0.701	0.543	0.693	0.000	0.008	0.541	0.672	0.002	0.029
0.543	0.689	0.716	0.544	0.709	-0.001	0.007	0.542	0.690	0.002	0.027
0.543	0.719	0.727	0.545	0.721	-0.002	0.006	0.541	0.705	0.002	0.022
0.544	0.744	0.740	0.544	0.733	0.000	0.007	0.540	0.719	0.004	0.021
0.543	0.805	0.766	0.541	0.765	0.002	0.002	0.536	0.758	0.007	0.008
0.522	0.918	0.857	0.520	0.858	0.002	0.000	0.512	0.868	0.010	-0.011
0.476	1.000	1.000	0.474	1.000	0.002	0.000	0.475	1.000	0.001	0.000
T/K=283.15										
0.373	0.000	0.000	0.372	0.000	0.001	0.000	0.373	0.000	0.000	0.000
0.505	0.095	0.296	0.505	0.302	0.000	-0.006	0.527	0.326	-0.022	-0.030
0.590	0.194	0.438	0.590	0.438	0.000	0.000	0.615	0.454	-0.025	-0.016
0.672	0.368	0.566	0.672	0.558	0.000	0.008	0.686	0.554	-0.014	0.012
0.719	0.617	0.674	0.720	0.668	-0.001	0.006	0.723	0.653	-0.004	0.022
0.722	0.672	0.699	0.723	0.693	-0.001	0.006	0.725	0.678	-0.003	0.020
0.725	0.701	0.711	0.724	0.707	0.001	0.004	0.725	0.693	0.000	0.018
0.725	0.719	0.722	0.724	0.716	0.001	0.005	0.725	0.704	0.000	0.018
0.723	0.754	0.738	0.723	0.735	0.000	0.003	0.723	0.725	0.000	0.013
0.711	0.849	0.793	0.711	0.799	0.000	-0.007	0.708	0.797	0.003	-0.005
0.632	1.000	1.000	0.636	1.000	-0.004	0.000	0.638	1.000	-0.006	0.000
T/K=293.15										
0.513	0.000	0.000	0.513	0.000	0.000	0.000	0.512	0.000	0.001	0.000
0.694	0.112	0.303	0.694	0.306	0.000	-0.004	0.718	0.326	-0.024	-0.023
0.842	0.280	0.485	0.841	0.485	0.001	0.000	0.860	0.487	-0.018	-0.002
0.913	0.450	0.587	0.913	0.581	0.000	0.006	0.923	0.571	-0.010	0.016
0.936	0.547	0.634	0.936	0.626	0.000	0.008	0.942	0.614	-0.005	0.020
0.949	0.682	0.698	0.951	0.691	-0.002	0.006	0.952	0.681	-0.003	0.017
0.950	0.719	0.716	0.951	0.712	-0.001	0.004	0.951	0.703	-0.001	0.013
0.941	0.810	0.771	0.941	0.770	0.000	0.000	0.938	0.767	0.003	0.004
0.910	0.908	0.854	0.908	0.859	0.002	-0.006	0.903	0.862	0.007	-0.009
0.833	1.000	1.000	0.836	1.000	-0.003	0.000	0.839	1.000	-0.006	0.000

Table 3. Continued

Experimental data			PR EoS				CSD EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	${}^a\Delta P/\text{MPa}$	${}^b\Delta y_1$	P_{cal}/MPa	$y_{1,cal}$	${}^a\Delta P/\text{MPa}$	${}^b\Delta y_1$
T/K=303.15										
0.690	0.000	0.000	0.691	0.000	-0.001	0.000	0.689	0.000	0.001	0.000
0.887	0.099	0.257	0.887	0.261	0.000	-0.005	0.908	0.275	-0.021	-0.019
1.051	0.233	0.423	1.051	0.427	0.000	-0.005	1.071	0.430	-0.020	-0.007
1.194	0.471	0.582	1.190	0.577	0.004	0.005	1.195	0.567	-0.001	0.015
1.209	0.560	0.629	1.213	0.621	-0.004	0.008	1.216	0.611	-0.007	0.018
1.226	0.683	0.692	1.227	0.686	-0.001	0.006	1.227	0.679	-0.001	0.012
1.226	0.706	0.706	1.227	0.699	-0.001	0.007	1.226	0.694	0.000	0.012
1.222	0.760	0.737	1.222	0.734	0.000	0.003	1.220	0.730	0.002	0.007
1.184	0.882	0.831	1.183	0.835	0.001	-0.004	1.178	0.837	0.006	-0.006
1.141	0.944	0.901	1.139	0.909	0.002	-0.009	1.136	0.912	0.005	-0.011
1.079	1.000	1.000	1.080	1.000	-0.001	0.000	1.082	1.000	-0.003	0.000
T/K=313.15										
0.906	0.000	0.000	0.912	0.000	-0.006	0.000	0.909	0.000	-0.002	0.000
1.112	0.087	0.217	1.112	0.214	0.000	0.003	1.137	0.231	-0.025	-0.014
1.264	0.181	0.350	1.264	0.344	0.000	0.006	1.295	0.358	-0.031	-0.007
1.372	0.271	0.436	1.367	0.427	0.005	0.009	1.394	0.435	-0.022	0.002
1.455	0.382	0.516	1.456	0.506	-0.001	0.011	1.474	0.505	-0.019	0.011
1.507	0.480	0.576	1.509	0.565	-0.002	0.012	1.520	0.560	-0.013	0.017
1.546	0.593	0.638	1.546	0.631	0.000	0.008	1.550	0.622	-0.004	0.016
1.552	0.687	0.690	1.557	0.688	-0.005	0.002	1.555	0.680	-0.003	0.010
1.551	0.703	0.701	1.556	0.699	-0.005	0.003	1.554	0.691	-0.003	0.010
1.548	0.746	0.732	1.553	0.728	-0.005	0.004	1.548	0.721	0.000	0.011
1.536	0.833	0.792	1.527	0.795	0.009	-0.003	1.519	0.793	0.017	-0.001
1.477	0.920	0.878	1.470	0.883	0.007	-0.005	1.461	0.885	0.016	-0.007
1.366	1.000	1.000	1.372	1.000	-0.006	0.000	1.373	1.000	-0.007	0.000
T/K=323.15										
1.174	0.000	0.000	1.183	0.000	-0.009	0.000	1.177	0.000	-0.003	0.000
1.375	0.071	0.172	1.375	0.167	0.000	0.005	1.396	0.180	-0.021	-0.008
1.615	0.194	0.343	1.614	0.337	0.001	0.006	1.642	0.347	-0.027	-0.003
1.778	0.323	0.460	1.776	0.449	0.002	0.011	1.795	0.450	-0.017	0.010
1.892	0.475	0.562	1.893	0.550	-0.001	0.012	1.899	0.545	-0.007	0.017
1.936	0.585	0.628	1.938	0.619	-0.002	0.009	1.937	0.611	-0.001	0.017
1.948	0.669	0.679	1.952	0.673	-0.004	0.006	1.945	0.666	0.004	0.012
1.949	0.703	0.701	1.951	0.696	-0.002	0.005	1.942	0.691	0.007	0.010
1.940	0.777	0.751	1.936	0.751	0.004	0.000	1.923	0.747	0.017	0.004
1.911	0.834	0.796	1.910	0.799	0.001	-0.003	1.895	0.797	0.016	-0.001
1.832	0.928	0.891	1.828	0.896	0.004	-0.005	1.814	0.898	0.018	-0.007
1.708	1.000	1.000	1.720	1.000	-0.012	0.000	1.717	1.000	-0.009	0.000
T/K=333.15										
1.497	0.000	0.000	1.518	0.000	-0.021	0.000	1.501	0.000	-0.005	0.000
1.737	0.085	0.170	1.739	0.169	-0.002	0.001	1.773	0.182	-0.036	-0.013
2.085	0.251	0.368	2.087	0.391	-0.002	-0.023	2.103	0.373	-0.017	0.018
2.200	0.331	0.434	2.204	0.464	-0.004	-0.030	2.202	0.435	-0.003	0.029
2.306	0.431	0.504	2.307	0.534	-0.001	-0.030	2.292	0.504	0.014	0.030
2.398	0.598	0.613	2.395	0.631	0.003	-0.018	2.371	0.616	0.028	0.015
2.411	0.654	0.649	2.405	0.663	0.006	-0.015	2.377	0.656	0.034	0.007
2.411	0.685	0.670	2.407	0.683	0.004	-0.013	2.376	0.679	0.035	0.004
2.406	0.729	0.702	2.402	0.713	0.004	-0.011	2.369	0.713	0.037	0.000
2.386	0.790	0.750	2.381	0.759	0.005	-0.009	2.345	0.764	0.041	-0.005
2.342	0.855	0.809	2.337	0.819	0.005	-0.010	2.302	0.824	0.041	-0.005
2.230	0.925	0.887	2.257	0.896	-0.027	-0.009	2.230	0.900	0.000	-0.004
2.116	1.000	1.000	2.128	1.000	-0.012	0.000	2.118	1.000	-0.002	0.000

$${}^a\Delta P = P_{exp} - P_{cal}, \quad {}^b\Delta y_1 = y_{exp} - y_{cal}$$

Table 2. The absolute average relative deviations ($\Delta P/P$) between measured and calculated values from the data of REFPROP 6.01 [14] were 0.005 for propane and 0.008 for HFC-152a. The experimental data and the results of the correlation are reported in Table 3. This table lists the measured mole fraction of the liquid and vapor phases, pressures and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy), point by point. Fig. 2 shows the comparison of measured and calculated values with the PR and CSD EoSs for propane (1)+HFC-152a (2) at 268.15, 273.15, 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K.

The interaction parameters of the binary mixtures for each isotherm, the binary parameters of the NRTL model with the Wong-Sandler mixing rules, and the average absolute deviations of pressure (AAD-P, %) and average absolute deviations of vapor-phase

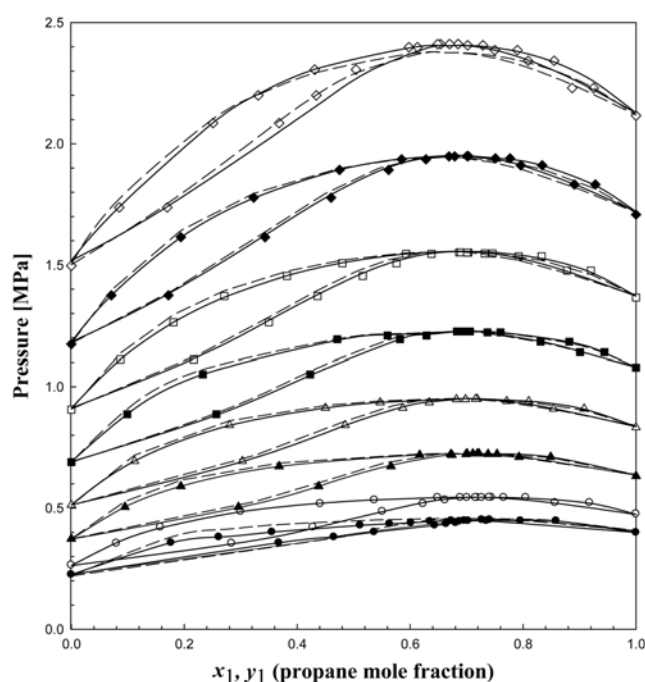


Fig. 2. P-x-y diagram for the propane (1)+HFC-152a (2) system. Experimental data at 268.15 K (●); 273.15 K (○); 283.15 K (▲); 293.15 K (△); 303.15 K (■); 313.15 K (□); 323.15 K (◆); 333.15 K (◇); calculated with the PR-EoS using W-S mixing (—); calculated with the CSD-EoS (---).

composition (AAD-y) between measured and calculated values are reported in Table 4. The average value of AAD-P (%) was 0.232%

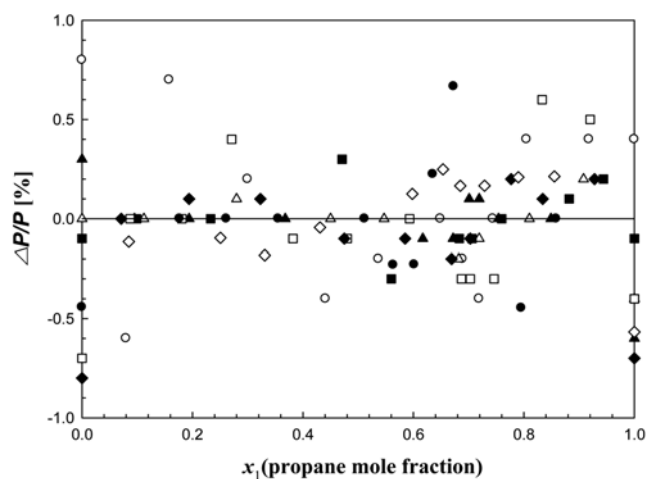


Fig. 3. Deviation of pressure for the system propane (1)+HFC-152a (2) from the PR-EoS using W-S mixing rule at 268.15 K (●); 273.15 K (○); 283.15 K (▲); 293.15 K (△); 303.15 K (■); 313.15 K (□); 323.15 K (◆); 333.15 K (◇).

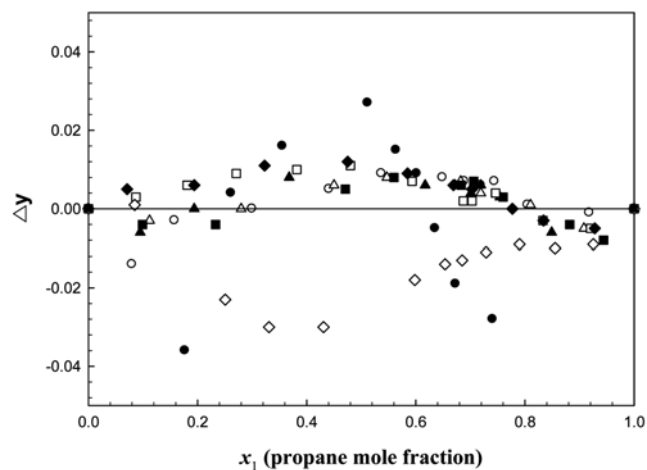


Fig. 4. Deviation of vapor composition for the system propane (1)+HFC-152a (2) from the PR-EoS using W-S mixing rule at 268.15 K (●); 273.15 K (○); 283.15 K (▲); 293.15 K (△); 303.15 K (■); 313.15 K (□); 323.15 K (◆); 333.15 K (◇).

Table 4. Values of binary parameters and average absolute deviations of P and y

T/K		268.15	273.15	283.15	293.15	303.15	313.15	323.15	333.15	
PR EoS	binary parameter	$^a k_{12}$	-0.6331	0.0686	0.0400	0.1214	0.1693	0.0680	0.1209	0.3678
		$^a \tau_{21}$	3.0376	0.7483	0.8874	0.6608	0.5805	0.6927	0.5087	0.8241
		$^a \tau_{12}$	3.3787	1.7013	1.4846	1.2219	0.9875	1.2293	1.1020	1.6753
		b AAD-P (%)	0.318	0.316	0.135	0.099	0.129	0.282	0.202	0.376
		c AAD-y	0.026	0.005	0.004	0.003	0.004	0.005	0.005	0.013
CSD EoS	binary parameter	f_{12}	0.1190	0.1401	0.1248	0.1244	0.1259	0.1363	0.1250	0.1201
		b AAD-P (%)	3.388	1.639	1.203	0.954	0.603	0.937	0.713	1.001
		c AAD-y	0.033	0.019	0.014	0.010	0.010	0.008	0.007	0.010

^aThe unit of k_{12} , τ_{21} and τ_{12} is dimensionless. $\tau_i = A_{ji}/(RT)$. (The unit of A_{21} and A_{12} is kcal/mol). ^b AAD-P (%) = $(1/N) \sum (P_{exp} - P_{cal})/P_{exp} \times 100$.

^c AAD-y = $(1/N) \sum (y_{exp} - y_{cal})$

and AAD-y was 0.008 for the PR EoS and 1.305% and 0.014 for the CSD EoS, respectively. Both AAD-P and AAD-y values of the

Table 5. Azeotropic Data (temperatures, pressure and mole fraction)

T/K	P/MPa	x_1 (propane mole fraction)
268.15	0.450	0.741
273.15	0.544	0.731
283.15	0.725	0.718
293.15	0.950	0.710
303.15	1.227	0.702
313.15	1.552	0.697
323.15	1.949	0.693
333.15	2.411	0.685

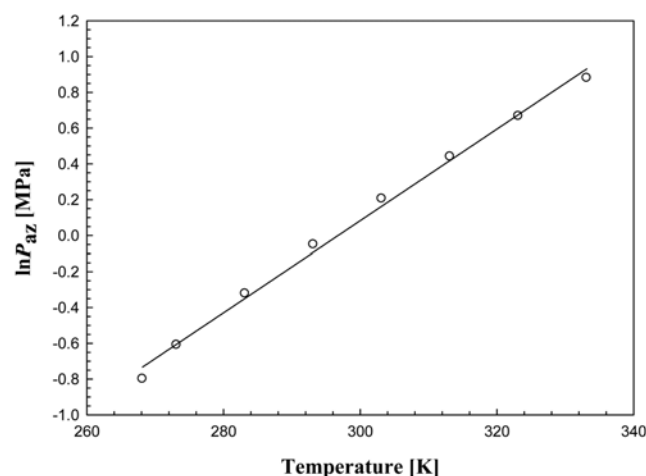


Fig. 5. Variation of the azeotropic pressure with temperature for the propane (1)+HFC-152a (2) system. The equation of the fitted line is $\ln P_{az} [\text{MPa}] = 0.0256 T [\text{K}] - 7.5975$ ($333.15 \text{ K} \geq T \geq 268.15 \text{ K}$).

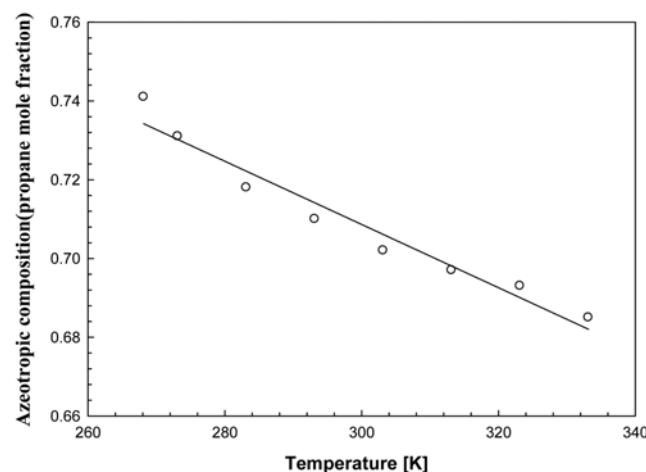


Fig. 6. Variation of the azeotropic composition with temperature for the propane (1)+HFC-152a (2) system. The equation of the fitting line is $x_{1,az} = -0.0008 T [\text{K}] + 0.9495$ ($333.15 \text{ K} \geq T \geq 268.15 \text{ K}$).

PR EoS are less than those of the CSD EoS. So only the PR EoS based results are shown in Figs. 3 and 4. From these figures and the low average deviations of P and y, we conclude that the calculated values from using the PR EoS and the CSD EoS give good agreement with the experimental data; however, the PR EoS using the Wong-Sandler mixing rule shows slightly better results. This mixture exhibits azeotropes. Azeotropic data for this mixture have been determined at the composition between 0.685 and 0.741 mole fraction, and pressures between 0.450 and 2.411 MPa in the temperature range from 268.15 to 333.15 K. Azeotropic pressures and compositions are shown in Table 5 and Figs. 5 and 6, respectively. As can be seen in these figures, azeotropic compositions and pressures are temperature dependent. In the range of experimental temperatures, the azeotropic compositions were correlated by the empirical equation $x_{1,az} = -0.0008 T [\text{K}] + 0.9495$, and azeotropic pressure was correlated by the empirical equation $\ln P_{az} [\text{MPa}] = 0.0256 T [\text{K}] - 7.5975$. These equations were fitted within the temperature range from 268.15 to 333.15 K.

CONCLUSIONS

VLE data for binary systems of propane (1)+HFC-152a (2) were measured at eight temperatures of (268.15, 273.15, 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K) by using a circulation-type equilibrium apparatus. The experimental VLE data were correlated with the PR-EoS by using the W-S mixing rule and the CSD-EoS. Calculated results with these equations have given satisfactory results in the comparison with the experimental data. In each case, the better results were obtained with the PR-EoS using W-S mixing rule. This system shows strong positive azeotropes for all the temperature range studied here.

ACKNOWLEDGMENT

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NOMENCLATURE

- a(T) : temperature-dependent constant of EoS
- A : adjustable parameters of NRTL model [kJ/g-mol]
- b : molecular volume [l/g-mol]
- g : an energy parameter [kJ/g-mol]
- f : CSD parameter
- k : PR EoS parameter
- N : the number of components in mixture
- P : pressure [MPa]
- R : gas constant, 8.3144 [J/mol·K]
- T : temperature [K]
- V : molar volume [l/g-mol]
- x : liquid mole fraction
- y : vapor mole fraction

Greek Letters

- α : attraction parameter
- Δ : deviation
- τ : dimensionless form of A/RT
- ω : acentric factor

Subscripts

- c : critical property
cal : calculated
exp : experimental
i, j : ith and jth components of the mixture
azeo : azeotropic point
m : mixtures
r : reduced property

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